

SIMULATION OF RHEOLOGICAL BEHAVIOR OF SECONDARY POLYMER FEEDSTOCK IN THE PRESENCE OF INORGANIC FILLERS UNDER CONDITIONS CORRESPONDING TO PROCESSING OF POLYMERS BY EXTRUSION AND DIE CASTING

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ABSTRACT

This work discusses simulations of rheological behavior of polymer feedstock, under conditions corresponding to polymer processing by extrusion and die casting, on the basis of data obtained by analysis of viscosity of composite melt in the oscillation range from 0.01 to 100 Hz. The considered compositions were based on secondary polypropylene and inorganic fillers (chalk additive and aluminum silicate spheres) and produced by pressing and die casting. Rheological properties of the polymer composition melts were evaluated by a HaakeMarsIII rheometer. It is established that all considered compositions are non-Newtonian, viscoelastic, pseudoplastic fluids, the viscosity of which decreases with the increase in oscillation frequency. Since in the range from 0.01 to 100 Hz the experimental viscosity variations as a function of oscillation frequency are rectified well in logarithmic coordinates, it becomes possible to derive approximation equations for prediction of melt viscosity under conditions corresponding to processing of polymers by extrusion and die casting (about 10,000 Hz). Correlation between the calculated viscosities and experimentally determined elastic modulus of the prepared compositions has been shown.

KEYWORDS: Secondary Polypropylene, Processing Of Polymers, Rheological Studies & Inorganic Filler

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INTRODUCTION

It is known that polymer composite materials (PCM) attract the highest attention with regard to further modification and possible wide scale application [1]. The PCM are based on polymer binders modified by various additives [2–4] including inorganic matters. Inorganic fillers are used mainly for decrease in shrinkage, residual strains and propensity for cracking as well as improvement of strength properties [5]. Each filler is characterized by peculiar features. For instance, chalk is one of the cheapest mineral fillers, it can be easily processed [6]. Kaolin significantly improves viscosity, increases elastic modulus, improves electric properties and moisture resistance

[7]. Talc is characterized by low abrasiveness, provides increased rigidity to composites and, contrary to other disperse fillers, does not decrease impact toughness [8–10]. A particular group of disperse fillers is comprised of microspheres, which are hollow spherical particles with the diameters from 10 to 2,000 μm and the wall thickness from 2 to 10 μm . Glass and aluminum silicate microspheres are used more frequently [11, 12].

However, addition of fillers to polymer composition can impact negatively processability of polymer feedstock, especially under conditions corresponding to processing of polymers by extrusion and die casting.

It is known that during extrusion, the range of shear rates varies usually from 0.01 to 1,000 s^{-1} : it is different upon melt flow along screw core, upon agitating flow perpendicular to core axis, and upon reverse flow from any flight to leading grooves [13–15]. At various stages of filling of injection molding machine there is no any single shear rate but, instead, a range of shear rates, frequently covering more than four orders of magnitude: injection via extrusion nozzle of capillary type – up to 10,000 s^{-1} , flow upon mold filling – about 100–300 s^{-1} .

Behavior of molten polymer at oscillation frequencies of about 0.01–100 Hz (or angular velocities of about 0.03–300 s^{-1}) can be determined experimentally using an up-to-date rheometer [16]. However, in order to obtain entire understanding of rheological properties of polymers, it is required to have its flow curve upon variation of shear rate in the range of three–four orders of magnitude. None of the available instruments can execute measurements in such wide range of shear rates. In this regard, it is required to simulate rheological behavior of polymer feedstock under conditions corresponding to polymer processing by extrusion and die casting; this is the target of this work. The considered composite material was based on secondary propylene (SPP) corresponding to primary H-350FF/3polypropylene.

METHODS

A sample of SPP corresponding to primary H-350FF/3polypropylene was used in this work. SPP sample was made of crushed material of substandard items produced by die casting. Chalk additive and aluminum silicate microspheres were used as inorganic fillers.

The compositions were produced by two methods:

- Extrusion using an AutoMH-NE automatic hydraulic press (Carver, USA) at 210°C and holding under 7,000 kgf in 3 min (referred to as extrusion). Preliminary the composition was mixed using a PlastographEC laboratory installation (Brabender, Germany) in 15 min under 200 N;
- Die casting using a Babyplast injection molding machine of horizontal type with injection volume up to 15 cm^3 (referred to as die casting). Similar to the extrusion, the compositions were also preliminary mixed using a PlastographEC laboratory installation (Brabender, Germany) in 15 min under 200 N.

Rheological measurements of molten SPP and filled materials on its basis were carried out using a Haake Mars III dynamic rheometer at 220°C in the oscillation frequency range from τ 0.01 to 100 Hz.

Physicomechanical properties of polymer composites were detected according to Russian standard GOST 11262-80, using a Shimadzu AGS-X tearing machine (Shimadzu, Japan).

It is known that when fluid is purely viscous and obeys the Newton flow law, the viscosity η is constant depending neither on shear rate nor on oscillation frequency f [13], that is, $\eta \sim af^0$, where a is the constant. However, rather frequently fluid does not obey the Newton law. For instance, upon flow of dilatant fluids their viscosity increases with the increase in oscillation frequency as $\eta \sim f^n$, where the exponent is $n > 0$. On the contrary, pseudoplastic fluids are characterized by decrease in viscosity with the increase in oscillation frequency, and the exponent n in the equation of viscosity as a function of oscillation frequency is $n < 0$. Numerous polymer solutions and melts are characterized by properties of pseudoplastic fluids.

As the experiments demonstrated, all considered compositions are non-Newtonian, viscoelastic, pseudoplastic fluids, their viscosity decreases with the increase in oscillation frequency.

Herewith, during the increase in content of inorganic additive in the composition, the melt viscosity varies (Figure 1), and it varies differently in compositions produced by different methods. In the case of compositions filled with chalk additive the differences in viscosity determined for compositions produced by extrusion and die casting are not so important, and in the case of compositions with aluminum silicate microspheres with high content of inorganic component, the difference is quite significant.

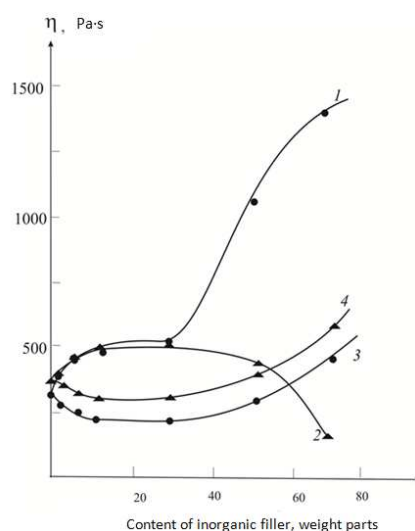


Figure 1: Complex Viscosity of Molten Compositions Obtained By Extrusion (1,3) and Die Casting (2,4) Based on SPP with Aluminum Silicate Microspheres (1,2) and Chalk Additive (3,4) Determined at Oscillation Frequency of 0.01 Hz As a Function of Filler Content

Unfortunately, viscosities determined at low oscillation frequencies are far from reflecting actual processing conditions of composites. However, if to determine viscosity as a function of oscillation frequency, it is possible to simulate behavior of molten polymers in the range of shear rates at which polymers are processed by extrusion and die casting.

Since in the experimental range of oscillation frequencies from 0.01 to 100 Hz, the experimental viscosity variations are rectified well in logarithmic coordinates, it becomes possible to derive approximation equations in the following form:

$$lg\eta = n * lgf + lga.$$

The obtained values for compositions based on SPP filled with inorganic matters are summarized in Tables 1 & 2.

Table 1: Simulated Data of Rheological Experiment in Oscillation Mode Performed with Secondary Polymer Feedstock in the Presence of Aluminum Silicate Microspheres, under Conditions Corresponding to Processing of Polymer by Extrusion and Die Casting

Content of Inorganic Additive in the Composition, wt %	Approximation Equation $lg\eta = n * lgf + lga$	Calculated Viscosity at Oscillation Frequency $f=10000$ Hz
Composition Produced by Extrusion		
2	$lg\eta=-0.152 f+2.377$	58.3
5	$lg\eta=-0.152 f+2.408$	63.1
15	$lg\eta=-0.152 f+2.427$	65.9
30	$lg\eta=-0.155 f+2.481$	72.8
50	$lg\eta=-0.157 f+2.570$	87.5
70	$lg\eta=-0.191 f+2.709$	88.1
Composition Produced by Die Casting		
2	$lg\eta=-0.128 f+2.361$	70.63
5	$lg\eta=-0.129 f+2.380$	73.1
15	$lg\eta=-0.133 f+2.378$	70.1
30	$lg\eta=-0.135 f+2.372$	67.9
50	$lg\eta=-0.136 f+2.376$	67.9
70	$lg\eta=-0.104 f+1.999$	38.3

Table 2: Simulated Data of Rheological Experiment in Oscillation Mode Performed with Secondary Polymer Feedstock in the Presence of Chalk Additive, under Conditions Corresponding to Processing of Polymer by Extrusion and Die Casting

Content of Inorganic Additive in the Composition, wt %	Approximation Equation $lg\eta = n * lgf + lga$	Calculated Viscosity at Oscillation Frequency $f=10000$ Hz
Composition Produced by Extrusion		
2	$lg\eta=-0.120 f+2.228$	55.9
5	$lg\eta=-0.125 f+2.266$	58.3
10	$lg\eta=-0.123 f+2.287$	62.4
30	$lg\eta=-0.110 f+2.278$	62.9
50	$lg\eta=-0.108 f+2.228$	68.5
70	$lg\eta=-0.117 f+2.369$	79.9
Composition Produced by Die Casting		
2	$lg\eta=-0.141 f+2.312$	54.1
5	$lg\eta=-0.144 f+2.309$	55.9
10	$lg\eta=-0.148 f+2.349$	57.1
30	$lg\eta=-0.149 f+2.373$	59.9
50	$lg\eta=-0.135 f+2.348$	64.2
70	$lg\eta=-0.133 f+2.365$	68.1

With the approximation equations, it is possible to simulate rheological behavior of molten polymers under such oscillation frequencies (shear rates) at which viscosity cannot be experimentally determined, but which correspond to actual processing conditions of polymer composites. Calculated viscosities are summarized in Tables 1 and 2, their variations as a function of content of inorganic component are illustrated in Figure 2.

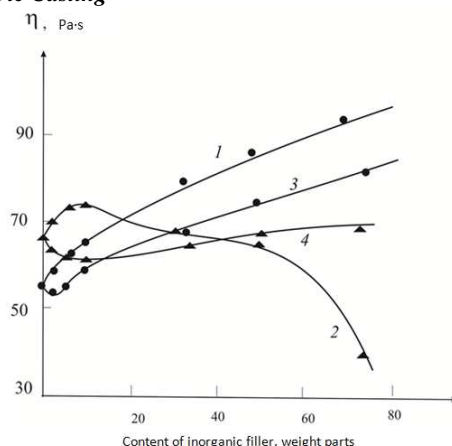


Figure 2: Complex Viscosity of Molten Compositions Obtained by Extrusion (1, 3) and Die Casting (2, 4) Based on SPP with Aluminum Silicate Microspheres (1, 2) and Chalk Additive (3, 4) Determined at Oscillation Frequency of 10000 Hz as a Function of Filler Content

It should be mentioned that, similar to the case of experimentally determined viscosities at oscillation frequency of 0.01 Hz, the complex viscosities calculated at oscillation frequency corresponding to processing of polymer compositions by extrusion and die casting (10000 Hz) depend on the method of composition production, especially with high amount of aluminum silicate microspheres.

Variations in rheological behavior of composites under conditions corresponding to processing are reflected upon physicochemical analysis of these materials. Thus, Figure 3 illustrates elastic modulus of compositions produced by extrusion and die casting with chalk additive and aluminum silicate microspheres. Correlation with the viscosities illustrated in Figures. 1–2 is obvious. It can be seen that exactly for the compositions with high amount of aluminum silicate microspheres produced by extrusion and die casting; the variations of elastic moduli are significant. Hence, it is highly important that there exists interrelation between calculated (simulated) viscosities obtained in oscillation mode and actual experimental data of deformation and strength properties of compositions.

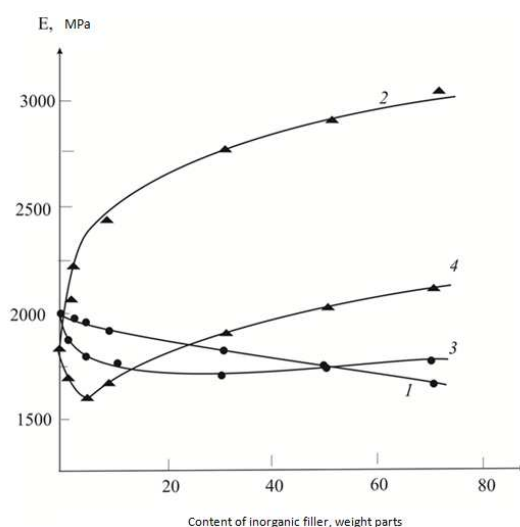


Figure 3: Elastic Modulus of Compositions Obtained by Extrusion (1, 3) and Die Casting (2, 4) Based on SPP with Aluminum Silicate Microspheres (1, 2) and Chalk Additive (3, 4) as a Function of Filler Content

Therefore, on the basis of rheological measurements carried out in certain range of shear rates (oscillation frequencies), it is possible to predict rheological behavior of composition under conditions corresponding to processing of polymer composites by extrusion and die casting, and to forecast the set of physico-mechanical properties.

CONCLUSIONS

It has been established during the experiments that the compositions based on secondary polypropylene behave as non-Newtonian, viscoelastic, pseudoplastic fluids, the viscosity of which decreases with the increase in oscillation frequency. It has been demonstrated that the compositions produced by extrusion and die casting are characterized by various viscosity, especially in the case of high content of aluminum silicate microspheres. The derived approximation equations make it possible to predict the melt viscosity under conditions corresponding to processing of polymers by extrusion and die casting. Correlation between the calculated viscosities and experimentally determined elastic modulus of the prepared compositions has been shown.

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